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ABSTRACT

Recently developed new fungicidal treatments for cotton goods, based on copper borate-zirconyl acetate and copper borate-zirconyl ammonium carbonate complex solubilization, required wet gravimetric analytical procedures to estimate copper and zirconium add-ons in the treated fabrics. Although X-ray fluorescence methods have given reasonably good results, this method is not available to the average mill, and suitable wet procedures were required to make these estimations universally available. This publication presents the wet gravimetric analytical procedures developed at the Southern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

Trade names and company names are included for the benefit of the reader and does not infer any endorsement or preferential treatment of the product listed by the U. S. Department of Agriculture.

ANALYTICAL PROCEDURES FOR COPPER AND ZIRCONIUM ON COPPER-ZIRCONIUM FUNGICIDES (GRAVIMETRIC)

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INTRODUCTION

Work involving the development of new fungicides and methods of application at the Southern Utilization Research and Development Division of Agricultural Research Service, resulted in two new types of fungicides, based on the formation of water soluble complex compounds with certain potentially fungicidal metal salts and zirconyl acetate and zirconyl ammonium carbonate.[2] The utility of these aqueous compounds is based upon control of the concentrations of metal salt and zirconium in application to fabrics. These copper borate-zirconium fungicidal treatments became interesting to the textile industry, and suitable methods were requested for the estimation of copper and zirconium.[3]

In the early stages of the work, X-ray fluorescence was used to determine these values.[4] However, this method showed some inconsistency due to difficulty in standardization, and also required specialized equipment. Consequently, wet analytical procedures were desirable, where consistency and accuracy can be readily verified. Attention was then turned toward development of such procedures, since literature is rather scarce with regard to zirconium analyses in the presence of organic materials and other metal ions. Colorimetric procedures, based upon zirconia "lake" formations with alizarine derivatives are reported in the literature.[5] These methods are interfered with by many metal ions, and demonstrate error possibilities through color shade variations and translucency of the test solutions in many instances. A good gravimetric procedure suggested the best accuracy, where chemical reaction isolates the desirable component, and precipitation assures estimation by weight. In line with this reasoning, the procedures in this paper were developed through chemical technology involving the chemical reactivity of both copper and zirconium, relative to gravimetric estimation.

MATERIALS AND METHODS

Chemicals

Zirconal acetate, a clear, yellowish-white solution containing 13 percent ZrO_2 and 12 percent free acetic acid, was obtained from Titanium Alloy Manufacturing Division of the National Lead Co. The compound is also available with 22.0 percent ZrO_2 and 12 percent acetic acid.

Zirconyl ammonium carbonate solution (10 percent ZrO_2), a water-white liquid with a moderately strong odor of ammonium carbonate, was obtained from Titanium Alloy Manufacturing Division of the National Lead Co.

Copper borate (Meta) is commercially available from the Shepherd Chemical Co., as a light blue powder of 40 percent copper metal content.

Hydrochloric acid was Reagent Grade, 36 to 38 percent HCl content, commercially available acid (Sp. Gr. 1.185).

Nitric acid was Reagent Grade, 70.5 percent HNO_3 content, commercially available acid (Sp. Gr. 1.422).

Ammonium hydroxide was Reagent Grade, 29 to 30 percent NH_4OH, commercially available base (Sp. Gr. 0.90).

Acetic acid (Glacial) was Reagent Grade, 99.8 percent CH_3COOH, commercially available acid.

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[1] One of the laboratories of the Southern Utilization Research and Development Division, Agricultural Research Service, U.S. Department of Agriculture.

[2] Conner, C. J., Cooper, A. S., Jr., Reeves, W. A., and Trask, B. A. Textile Res. Jour. 34 (4): 347-357. 1964.

[3] Letters from textile mills (1964-1965).

[4] Tripp, V. W., Piccolo, B., Mitcham, D., and O'Connor, R. T. Testile Res. Jour. 34 (9): 773-777. 1964.

[5] Feigl, F. Spot Tests in Inorganic Analysis, pp. 199-204. 1958.

Sulfuric acid (36 N) was Reagent Grade, 96 to 97 percent H_2SO_4, commercially available acid (Sp. Gr. 1.84).

Sodium thiosulfate ($Na_2S_2O_3 \cdot 5H_2O$) was Reagent Grade, granulated, and commercially available.

Apparatus

Porcelain crucibles--Coors No. 1 or No. 2 type.

Filter paper--Whatman No. 40, analytical-ashless (11.5 cm.).

Glass funnels--3 in. diameter, with long stem.

Pyrex beakers--250 ml. and 600 ml. (Griffin type).

Analytical balance--Mettler or comparable.

Wash bottle, stirring rods, spatulas, Meker burner triangle, ring and stand, watch glasses, Hydrion pH paper, hot plate, and desiccator.

Fabrics

The cotton fabric used in these evaluations was desized, scoured, and equivalent to an 8-oz. army duck, although any fabric composed of organic fiber is suitable for the procedures.

Copper borate-zirconyl acetate and copper borate-zirconyl ammonium carbonate fungicides were applied to the cotton fabric by conventional padding, drying, and curing, to give a theoretical copper and zirconium add-on.[6]

The theoretical add-on is based upon the concentration of copper and zirconium in solutition and the percent wet pickup by the treated fabric. For example, with 0.8 percent copper and 4.50 percent zirconia (ZrO_2) in solution, and a 60 percent wet pickup is determined by weight gain after padding, the theoretical add-ons would be 0.48 percent copper and 2.70 percent zirconia. Although this appears sound from a theoretical viewpoint, variations can occur because of the following:

(1) Variation in wet pickup over different areas of the treated fabric relative to fabric construction and roll pressure.

(2) Actual chemical assay different from the theoretical assay with regard to the chemicals used.

(3) Separation of some copper and zirconium in the padding bath due to hydrolysis and loss of ammonium carbonate (dissociation into NH_3 and CO_2).

(4) Migration of the wet material in the fabric drying and curing.

(5) Evaporation of solution during padding to give actually higher percent add-ons with an apparently lower weight gain of wet padded fabric.

These variations warrant an actual analysis of the cured fabric to establish the actual copper and zirconium content. Consequently, X-ray fluorescence analyses were made. The results were found to vary, and this was attributed to the presence of interference elements and the standards used. The method also required considerable sample preparation and procedure, as well as highly specialized equipment.[7]

The wet gravimetric procedure is based on zirconia insolubility and cuprammonium complex ion solubility, in separating the two elements, after removal of all organic material through ignition. The analytical steps were worked out on paper and evaluated through numerous laboratory procedures. The procedure is initiated with the ignition of the treated fabric sample to remove all organic matter and carbon, which leaves the mineral components as an ash. The ash is selectively treated with mineral acid to dissolve the copper and leave the zirconia as an insoluble residue. The zirconia is quantitatively estimated as such (ZrO_2), while the separated copper is eventually precipitated as sulfide (CuS) and ignited to the oxide (CuO), when the copper oxide is converted to copper metal by factor. Basing the copper metal and zirconia content upon the original weight of treated fabric sample, the percentages of both copper and zirconia are determined. The following steps outline the method of procedure as used:

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[6] See footnote 2.

[7] See footnote 4.

(1) A representative section of treated fabric was chopped or clipped into small squares approximately 3/8 to 1/2 inch square. A 2.0 to 2.5 gram sample of the material was weighed into a Coors No. 1 or No. 2 porcelain crucible. The crucible had been previously weighed after desiccation. Weighings were made to the fourth place.

(2) The crucible and sample were placed in a triangle on a ring and stand and ignited with a Meker burner to white heat for 1 hour or more, until a carbon-free mineral ash remained. This was allowed to cool to room temperature.

(3) Forty-five ml. of concentrated hydrochloric acid (Sp. Gr. 1.185) were mixed with 15 ml. of concentrated nitric acid (Sp. Gr. 1.422) to make 60 ml. of Aqua regia in a 250 ml. Pyrex beaker. The crucible with copper-zirconia ash was placed in the acid, on its side, so as to wet the mineral ash thoroughly.

(4) The beaker, curcible, and ash were placed on the hot plate and heated slowly to a boil to digest the ash for 30 minutes.

(5) At the end of this time, the crucible was lifted out of the acid with the end of a stirring rod and washed thoroughly (wash bottle) inside and outside and the washing returned to the acid.

(6) The diluted acid in the beaker contained the ZrO_2 as a white precipitate, while the copper remained in solution as cupric chloride. The total digestion products and wash water should be approximately 75 ml.

(7) The ZrO_2 was filtered off through a No. 40 Whatman ashless paper and washed three times with water to remove all acid and soluble salts. The washings were included with the copper containing filtrate.

(8) The paper with ZrO_2 was ignited in a weighed Coors No. 1 crucible until only the mineral ash remained. The crucible was cooled in a desiccator, weighed, and reignited, and weighed after desiccation--until constant weight was attained.

(9) The percent ZrO_2 was calculated from the weight of ZrO_2 and weight of original sample fabric:

$$\frac{ZrO_2 \text{ gms.}}{\text{Wt. of fabric in gms.}} \times 100 = \text{percent}$$

ZrO_2 in the fabric.

(10) The filtrate, approximately 100 ml., contained copper as chloride and free mineral acids. The filtrate was transferred to a 600-ml. beaker, taking care to rinse the 250-ml. beaker with distilled water, and adding the washings to the 600-ml. beaker, taking care to rinse the 250-ml. beaker with distilled water, and adding the washings to the 600-ml. beaker.

(11) Ammonium hydroxide (29.9 percent) was added slowly to the filtrate until an excess of the reagent was present. This can be confirmed by the formation of the deep blue cuprammonium ion, the strong odor of ammonia, and a pH range of 10.0 to 11.0.

(12) The excess ammonium hydroxide was neutralized to a pH of 7.0 to 7.5 with glacial acetic acid (99.8 percent).

(13) A 9 N sulfuric acid solution was prepared from concentrated 36 N sulfuric acid by mixing one part of the acid with three parts of distilled water. Ten ml. of 9 N sulfuric acid were added to the neutralized filtrate.

(14) Five grams of sodium thiosulfate were dissolved in 300 ml. of distilled water, and this solution added to the acidified filtrate in the 600-ml. beaker to give a total volume between 450 and 475 ml.

(15) The 600-ml. beaker was placed on the hot plate and allowed to come to a boil. Copper precipitated as sulfide in conjunction with free sulfur. Boiling was continued for 15 minutes. This was followed by removal of the beaker from the plate. The beaker was covered with a watch glass and allowed to stand overnight. On standing, all solids settled to the bottom of the beaker.

(16) The contents of the beaker were filtered through a No. 40 Whatman ashless paper. The paper and residue were washed free of soluble salts and acid and transferred to a weighed Coors No. 1 crucible.

(17) The paper and residue were ignited with a Meker burner until only the mineral residue (black) remained. The crucible was cooled, desiccated, and weighed to constant weight.

(18) The copper oxide determined by weight was converted to copper metal by multiplying by the factor 0.7988.

(19) The percent copper metal in the fabric was then calculated from the weight of copper, as based upon the weight of fabric sample:

$$\frac{\text{Wt. of Cu in gms.}}{\text{Wt. fabric in gms.}} \times 100 = \text{percent copper in fabric}$$

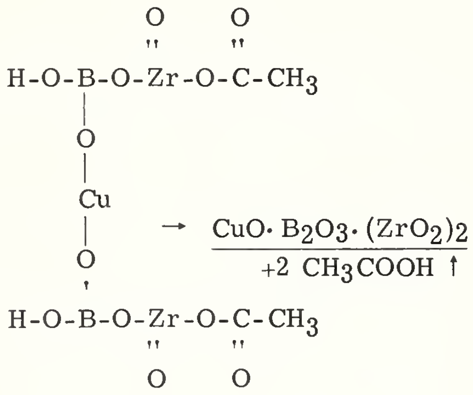
Theoretical Mechanisms and Explanations

(1) Ignition of treated fabric. Heat oxidation converts all organic matter to carbon dioxide, and water. Further ignition causes the carbon to sublime and oxidize to carbon dioxide, thus leaving the crucible. If basic zirconyl acetate is present, acetic acid is driven off and zirconia remains. Zirconia also remains from zirconyl ammonium carbonate treatments. The ignition reactions are as follows:

(a) $\text{Cellulose} + [0] \rightarrow CO_2\uparrow + H_2O\uparrow + C$

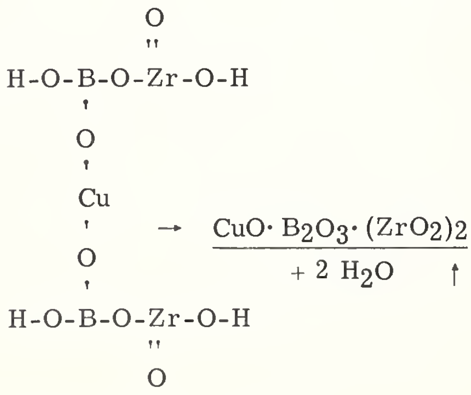
(b) $C + O_2 \rightarrow CO_2\uparrow$

(c)



$$\begin{matrix} H\text{-}O\text{-}B\text{-}O\text{-}Zr\text{-}O\text{-}C\text{-}CH_3 \\ | \\ O \\ | \\ Cu \\ | \\ O \\ | \\ H\text{-}O\text{-}B\text{-}O\text{-}Zr\text{-}O\text{-}C\text{-}CH_3 \end{matrix} \rightarrow \frac{CuO\cdot B_2O_3\cdot (ZrO_2)2}{+2\ CH_3COOH\uparrow}$$

(d)



$$\begin{matrix} H\text{-}O\text{-}B\text{-}O\text{-}Zr\text{-}O\text{-}H \\ | \\ O \\ | \\ Cu \\ | \\ O \\ | \\ H\text{-}O\text{-}B\text{-}O\text{-}Zr\text{-}O\text{-}H \end{matrix} \rightarrow \frac{CuO\cdot B_2O_3\cdot (ZrO_2)2}{+\ 2\ H_2O\uparrow}$$

The B_2O_3 remains in the mineral ash and is later converted to boric acid in acid digestion, followed by solubility in the wash water and filtrate.[8]

(2) Acid digestion. Converts the copper to cupric chloride, the B_2O_3 to boric acid, and leaves the ZrO_2 as an insoluble residue.[9]

(3) Ammonium hydroxide filtrate. Converts the copper to a complex cuprammonium ion and produces ammonium borate with any residual boric acid. All other free mineral acids are converted to ammonium salts.

(4) Neutralization with acetic acid and acidification with sulfuric acid. Ammonium acetate, produced by acetic acid neutralization, assures nonhydrolysis of the copper ion. Sulfuric acid converts copper to the sulfate, in which form it is suitable for sulfide precipitation. Sulfuric acid produces thiosulfuric acid with the sodium thiosulfate, which decomposes to produce hydrogen sulfide for the copper sulfide precipitation.

$$3\ (Na_2S_2O_3 + H_2SO_4 \rightarrow H_2S_2O_3 + Na_2SO_4)$$

(5) Copper sulfide and sulfur precipitation.

(a) $3\ H_2S_2O_3 + 3\ H_2O \xrightarrow{\Delta} 3\ H_2SO_4 + 3\ H_2S\uparrow$

(b) $2\ H_2S + O_2 \rightarrow 2\ H_2O + 2\ S\downarrow$

(c) $Cu\ SO_4 + H_2S \rightarrow Cu\ S\downarrow + H_2SO_4$

(6) Copper sulfide ignition. Ignition in air converts the copper sulfide to copper oxide--

$$Cu\ S + 3\ \ O \rightarrow Cu\ O + SO_2\uparrow$$

The residual sulfur precipitated with the copper sulfide also burns off by oxidation, which leaves only copper oxide:

$$2\ S + 2\ O_2 \rightarrow 2\ SO_2\uparrow$$

Results and Discussion

Determinations in duplicate check within 98 percent of each other. The method is excellent for zirconium in the absence of silica or silicates, where Aqua regia extractions would leave silica with the ZrO_2. If silicone finishes are to be applied over a copper-zirconium fungicide treatment, it would be necessary to perform these analyses prior to silicone finishing the treated fabric. if the zirconium value is desired. However, copper may be determined by the same procedure, with or without the presence of silicone compounds.

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[8] Lange, N. A. Handbook of Chemistry, p. 228, 1961.

[9] Lange, N. A. Handbook of Chemistry, p. 332, 1961.

In comparing this analytical procedure with X-ray fluorescence and another commercial procedure, samples of copper borate-zirconyl acetate (copper zirconyl boro-acetate) and copper borate-zirconyl ammonium carbonate (copper borato-zirconic acid) treated duck samples were analyzed by each of the three procedures for copper and zirconia.

Table 1 shows the comparative results obtained in each case. The theoretical add-on values were based on the wet pickup percentage in padding.

TABLE 1. --Analysis results with copper-zirconium treatments

	Theory		X-Ray		Commercial		New wet method	
	Cu	ZrO_2	Cu	ZrO_2	Cu	ZrO_2	Cu	ZrO_2
	Pct.	Pct.	Pct.	Pct.	Pct.	Pct.	Pct.	Pct.
Copper Borate Zirconium acetate	0.36	2.28	0.33	2.30	0.18	2.67	0.30	2.38
	0.35	2.17	0.32	2.57	0.23	2.71	0.30	2.60
	0.36	2.24	0.36	2.63	0.21	2.79	0.31	2.70
	0.35	2.17	0.32	2.43	0.23	2.69	0.31	2.56
Copper borate-zirconyl ammonium carbonate	0.45	2.81	0.49	2.56	0.22	2.77	0.46	2.98
	0.46	2.83	0.53	2.63	0.19	2.78	0.48	3.06
	0.47	2.95	0.54	2.84	0.16	2.65	0.48	3.03
	0.45	2.81	0.48	2.27	0.22	2.75	0.47	2.92

Table 1 shows the commercial results to be considerably off with regard to percent copper. This indicates an error or loss in some stage of their procedure, since the percentage variation seems to be rather constant and reflects only approximately one-half of the copper present. The X-ray method appears to run into trouble with zirconium estimation, showing "plus variations with the zirconyl acetate and "minus" variations with the zirconyl ammonium carbonate treatment. The new method shows a "plus" variation with both treatments, with very close results, as compared with theory, in the zirconyl ammonium carbonate treatments. The closest copper checks with theory were obtained by the new wet method, described in this paper, and the X-ray method. The table clearly shows that the wet method is comparable to X-ray, and possibly more accurate than X-ray.

Table 2 is based upon comparative results obtained with X-ray and the new wet method in the analysis of copper borate-zirconyl ammonium carbonate treatments for the U. S. Army Research Laboratories at Natick, Mass., relative to evaluations with copper-zirconium fungicides applied to cotton duck for rot resistance.

TABLE 2. --Comparative results obtained with wet pickup, X-ray, and new wet method in the analysis of copper borate-zirconyl ammonium carbonate.

Treatment	By wet pickup		X-ray method		New wet method	
	Cu	ZrO_2	Cu	ZrO_2	Cu	ZrO_2
	Pct.	Pct.	Pct.	Pct.	Pct.	Pct.
Copper borate-zirconyl ammonium carbonate	0.55	1.89	0.49	1.90	0.51	1.79
	0.58	3.61	0.74	4.55	0.77	4.59
	0.50	4.79	0.52	4.40	0.45	4.14

In Table 2 the wet analytical value for percent copper with the second sample was determined in duplicate with the values for copper being 0.76 percent in one case and 0.77 percent in the other. In the same analytical procedures, the zirconia (ZrO_2) values were 4.56 and 4.61 percent. These values for copper and zirconia show the results to be within 98 percent of each other. It will be noted that the rough pilot-plant weighings for wet pickup do not reflect the actual add-ons as compared with results obtained by X-ray and the new wet method, and reflected in the results obtained by both of these methods.

Since X-ray values have been obtained in certain instances where the results have varied, the new gravimetric method is a most effective means of checking and confirming X-ray fluorescence values. In several instances where X-ray values did not confirm the gravimetric results, the X-ray analysis was repeated. These repeated results did confirm the gravimetric results. Consequently, the new wet method technique is a practical and universally available laboratory means to estimating copper and zirconium together in any copper-zirconium fungicidal treatment.

Furthermore, the estimation of copper and zirconium in padding solutions may be obtained by evaporating a weighed sample of the solution to dryness, igniting the residue, and following the previously outlined analysis procedure. This has been successfully accomplished in the estimation of copper and zirconium in previously reported work with metal salt-zirconium fungicidal compounds.[10]

SUMMARY

Resulting from the need for a universal laboratory wet method for estimating copper and zirconia in copper-zirconium fungicidal treatments for cotton, a new method was worked out for the chemical gravimetric analyses of copper and zirconia when present together in these treatments. The method is based on ignition to remove all organic matter, which leaves a mineral ash composed of $CuO \cdot B_2O_3 \cdot (ZrO_2)_2$. *Aqua regia* extraction removes the copper but does not solubilize the ZrO_2, which is estimated as such after filtering, washing, and igniting. The copper is then converted to sulfate, followed by precipitation as sulfide (CuS), which is estimated as CuO by ignition, and converted to copper (Cu) by factor. The method was compared with X-ray fluorescence values and was demonstrated to be a practical and efficient method for use in all textile mills that have chemical laboratory facilities.

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(7) U. S. Patent 3,183,118.

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[10] U. S. Patent 3,183,118.